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Problems for the Advanced Physical Chemistry Student

Part 7, Phase Equilibrium

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 (Dated: June 9, 2008)

I. SYNOPSIS

This is a set of problems that were used near the turn of the century and which will be lost when the web site they were on disappears with my demise. Because these problems are being taken from the web and are being edited, their statements and the hints/answers offered are subject to the typical editorial errors that ensue when such work is undertaken in the vacuum of a non-teaching situation. Therefore, I claim any errors for myself, and hate to note that there most likely is no point in contacting me about them for obvious reasons.

II. GIBBS AND HELMHOLTZ FREE ENERGIES

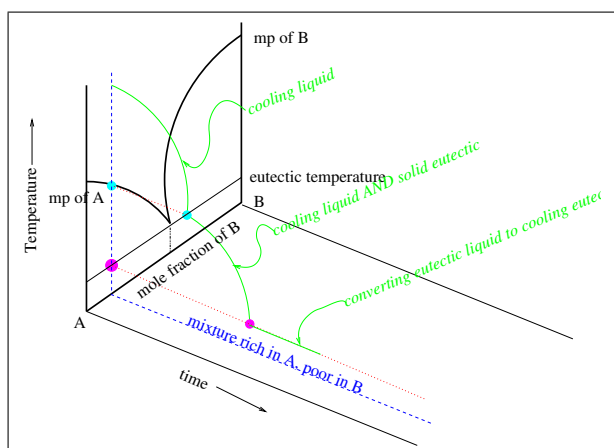


FIG. 1: Time-Temperature Cooling Curves construction of 2 component eutectic phase diagram.

1. The heat of fusion of ice is $79.7 \frac{\text{cal}}{\text{gram}}$ at 0°C and 1 atm. The density of ice is 0.9168 grams/cc and the density of water is 0.9999 gram/cc at 0°C . Calculate the melting point of ice at 325 atm (in $^\circ \text{C}$) Note: this question assumes that you will approximate the locus of coexisting phases with a straight line, using the average temperature over the domain in question!

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Answer and/or Hint

We know that

$$\frac{\Delta p}{\Delta T} = \frac{\Delta H^\circ}{T \Delta V}$$

so

$$\frac{\Delta p}{\Delta T} \equiv m = \frac{79.7}{(\sim 273) \left(\frac{18}{0.9999} - \frac{18}{0.9168} \right)}$$

in mixed units. We can convert calories to cc-atm or *vice versa*; the *calorie* is clearly an inferior choice. Note that the temperature should be the average between the melting point of ice at 325 atm and that of ice at 1 atm, so perhaps we need a cyclical solving procedure here.

Once we know the “slope” of the line, we have

$$p = p_0 + \frac{\Delta p}{\Delta T} \Delta T$$

$$p = p_0 + m \Delta T$$

i.e.,

$$325 = 1 + \frac{\Delta p}{\Delta T} (T - 273)$$

$$325 = 1 + m(T - 273)$$

provided the slope is in units of atm/K.

2. Ammonium nitrate undergoes a phase transition from one solid modification to another at 125.5°C at 1 atm, and at 135°C at 1000 atm. The form stable at the higher temperatures has an average volume of 0.0126 cc/gram greater than the other modification over the pressure range studied. Calculate the heat of transition (in cal/mole). Note: this question assumes that you will approximate the locus of coexisting phases with a straight line, using the average temperature over the domain in question!

 Answer and/or Hint

This is the same problem as the first one, different numbers, different phases, different unknowns, but, ho hum, still just the same.

3. AgI exists in two forms, α and β , which are in equilibrium at 146.5 C at 1 atm. For the change of α to β , the heat of transition is 1530 cal/mole, while the accompanying change in volume is -2.2 cc/mole. At what pressure (in atm) will the transition temperature be 145 C? Note: this question assumes that you will approximate the locus of coexisting phases with a straight line, using the average temperature over the domain in question!

 Answer and/or Hint

This is getting boring!

4. At a certain temperature, the vapor pressure of pure A is 108.0 and the vapor pressure of pure B is 55.8, both in mm. Hg. The vapor pressure of A (in solution) follows the equation Vapor Pressure of $p_A = 108 * (1 - 0.1 * x_B - 0.9 * x_B^2)$ and that of B follows the equation Vapor Pressure of $p_B = 55.8 * (0.2 * x_B + 0.8 * x_B^2)$. where ' x_B ' is the mole fraction of B in the solution. Calculate the mole fraction of A in the vapor (y_A) if the mole fraction (in solution) of A (x_A) is 0.638.

 Answer and/or Hint

We know that

$$p_A = 108 * (1 - 0.1 * x_B - 0.9 * x_B^2)$$

and

$$p_B = 55.8 * (0.2 * x_B + 0.8 * x_B^2)$$

so

$$p_{total} = p_A + p_B$$

and therefore

$$y_A = \frac{p_A}{p_{total}}$$

where y_A is the mole fraction of A in the vapor when the mole fraction of A in the liquid is x_A . The rest is trivial.

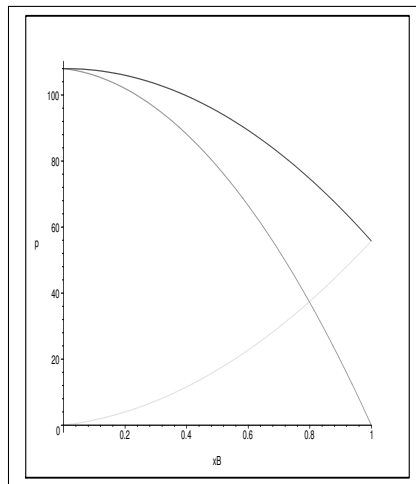


FIG. 2: The partial pressures of the two components, A and B, and the sum of the two (the total vapor pressure over the solution).

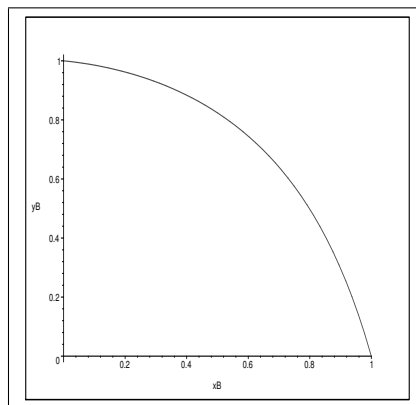


FIG. 3: The mole fraction (y) of B in the gas phase if the mole fraction of B in the liquid is x .

III. EPILOGUE

After editing this material for weeks, and continuously finding errors, some small, some huge, I have to wrap it up and send this off. If, in the years 2008-2010 or so, you come across an error, and you e-mail me, I will try to have it corrected.

But since this material is written in LaTeX there is some doubt whether or not I'll have access to a Linux machine, and access to the digitalcommons site. You can try; we'll see what happens, if anything. Thanks to all the students over the last 45 years who've taught me Physical Chemistry.